

Determination of Sulfur Trioxide in Engine Exhaust

by Dean R. Arnold*

Sulfur trioxide in the exhaust gas of an internal combustion engine is removed and concentrated by absorption in a solution of 80% isopropyl alcohol, which quantitatively absorbs it and inhibits the oxidation of any sulfur dioxide which may be absorbed. The absorbed sulfur trioxide (sulfuric acid) is determined by an absorption titration by using barium chloride as the titrant and thorin as the indicator. The sulfur dioxide content of the exhaust is measured continuously by means of a DuPont Model 411 ultraviolet photoanalyzer.

As the automobile manufacturers are using oxidation catalysts on a portion of their 1975 car production, it became necessary to consider the effect of these catalysts on emissions other than just carbon monoxide and hydrocarbons. One such emission is sulfur dioxide. Sulfur dioxide is produced in the combustion cycle of the engine by the oxidation of the sulfur which is present in the gasoline. Since one of the important uses of noble metal oxidation catalysts in the chemical industry is the production of sulfuric acid by oxidizing sulfur dioxide to sulfur trioxide, a serious emission product from catalyst-equipped vehicles may be sulfuric acid.

A large number of methods for analyzing sulfur trioxide emissions in stack gases is available in the literature. However, most of these methods suffer interferences from materials which are commonly found in internal combustion engine exhausts, such as ammonia and nitrogen oxides. One method,

that of Seidman (1), which does not have these interferences has been modified to determine sulfur trioxide emissions in engine exhausts.

Experimental

Apparatus

Four midjet impingers, three with orifice stems and one with a fritted glass stem, are used to collect the sulfur trioxide emissions.

A DuPont 411 photoanalyzer was used to measure the sulfur dioxide content of the sample gases. The 411 is a continuous flow ultraviolet analyzer which measures the absorbance of sulfur dioxide at 280 nm. A Texas Instruments dual channel recorder was used to obtain a record of the sulfur dioxide emissions.

Reagents

Isopropyl alcohol was reagent grade and was used as a solution of 80% by volume isopropyl alcohol in 20% distilled water.

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Barium chloride was 0.01N in 80% isopropyl alcohol; Thorin indicator, 0.2% in water.

Procedure

Sample Collection: The sampling train used for laboratory tests with cylinder gas samples may be depicted by the scheme (1):

Sample → Flowmeter → Impingers
→ SO₂ meter → Pump → Outlet (1)

To measure the sulfur dioxide coming out of this system, the DuPont analyzer was connected to the outlet of the impinger train with Tygon tubing. The incoming sulfur dioxide was calculated with the use of calibrated flowmeters and sampling through a bypass around the impingers directly into the DuPont analyzer.

Due to the high temperatures of actual engine exhausts, it was necessary to use a stainless steel probe inserted into the exhaust pipe. The probe was connected directly to the first impinger with Teflon tubing. This sampling system is as shown in eq. (2).

A system similar to that used for cylinder gas samples was used to handle samples that were collected in bags, similar to CVS bags, prior to analysis. Engine exhaust samples were collected by the stainless steel probe and injected directly into the bag through Teflon tubing. Prior to collecting the samples, the bags were partially filled with dry air to prevent any moisture condensation and absorption of sulfur trioxide. The bag analysis system was used to allow the collection of several different samples from one engine within a relatively short period of time. Another reason for using this system was to investigate the possibility of analyzing the CVS bags directly, either during or immediately after any CVS test.

Sulfur Trioxide Analysis: Four midget impingers are connected in series by Tygon tubing. The first three absorbers, having orifice stems, are filled with 15 ml of 80% isopropyl alcohol. A small amount (2–3 ml) of 80% isopropyl alcohol is added to the fourth absorber which has a fritted glass stem. This small amount of solution in the fourth absorber is sufficient to keep the fritted glass moist and to aid in retaining any solution or sulfur trioxide which may escape from the first impingers. All of the impingers are immersed in an ice water-salt solution.

The gas sample is drawn into the impingers by a pump operating at a flow rate of less than 10 ft³/hr for a time sufficient to pass at least 3 ft³ of gaseous sample through the system. When possible, at least 5 ft³ of sample is used.

After collecting the sample, the absorbers and all connecting tubing are rinsed into a 100-ml volumetric flask and diluted to volume with 80% isopropyl alcohol. Five drops of thorin indicator are added to a 25-ml aliquot of this solution and titrated with 0.01N barium chloride to the pink endpoint. The determination should be completed within 1 hr after sampling is complete to eliminate possible errors which may arise if any sulfite oxides to sulfate. If the determination cannot be carried out immediately, dry nitrogen should be drawn through the system for 10–15 min.

Sulfur Dioxide Analysis: A portion of the exhaust sample is drawn into the DuPont analyzer by splitting the sample stream in front of the impingers or by using a separate probe. The amount of sulfur dioxide being emitted is calculated from the area of the curve generated by the recorder which is connected to the DuPont Analyzer.

Exhaust → Probe → SO₂ Meter → Flowmeter → Pump → Outlet
→ Impingers → Flowmeter → Pump → Outlet (2)

Interferences

Exhaust Gas Components: A series of experiments was conducted to determine if the analysis method responded to any other component in the exhaust by using cylinder gas mixtures. Gas mixtures were prepared which contained various amounts of nitric oxide, nitrogen dioxide, oxygen, propane, water vapor, and sulfur dioxide. These mixtures were heated to various temperatures, up to 600°C, before being passed through the absorption impingers. No detectable amount of sulfur trioxide was found to be present upon analysis of the resulting solutions.

As an actual engine exhaust is much more complicated, a larger series of experiments was conducted in which the exhaust gas from a single cylinder engine was used. The exhaust from a single cylinder engine operating on isooctane, which contains no sulfur, was analyzed both before and after it had passed through a hot noble metal catalyst. In neither case was it possible to detect sulfur trioxide.

The possible interferences of particulates in the exhaust were investigated by adding particles obtained from the inside of an actual exhaust pipe to an 80% isopropyl alcohol solution and then analyzing for sulfur trioxide. Titration of this sample showed no detectable sulfur trioxide. Analysis of an engine exhaust sample collected by impingers containing some of this particulate material showed only 40% of the sulfur trioxide that was found under identical conditions using impingers did not contain any particulate material.

Oxidation of Sulfur Dioxide to Sulfur Trioxide: When operating a single-cylinder engine on gasoline with a high sulfur content, sulfur trioxide was detected in the exhaust prior to its passing through a catalyst.

A series of experiments was carried out to determine whether sulfur dioxide was being oxidized in the exhaust or sampling systems.

To check possible oxidation in the exhaust system sulfur dioxide was added to the exhaust of a single-cylinder engine running on isooctane. Analysis of the resulting gas mixture indicated no sulfur trioxide.

To find out if oxidation was occurring in the sample probe, a known quantity of sulfur dioxide was injected into the front of the probe attached to the exhaust system of an engine operating on isooctane. The sulfur dioxide was not injected until the probe reached the temperature of the exhaust system. No sulfur trioxide was detected.

To check on the possibility of oxidation in the impingers, an isooctane exhaust and sulfur dioxide were introduced into the impingers simultaneously by means of a Y connector at the inlet of the first impinger. Analysis of this sample showed no oxidation of sulfur dioxide to be occurring.

Results

As an actual engine exhaust is very complex, this analysis procedure has been investigated in detail to determine whether there are any interferences due to the various exhaust gas components, or to the sampling system itself. All of the various tests performed with artificial exhaust gas mixtures or the exhaust gas from an engine operating on isooctane fuel failed to indicate any interferences. Similarly, the tests where sulfur dioxide was injected into the exhaust and sampling system at various points did not indicate the possible oxidation of sulfur dioxide to sulfur trioxide.

REFERENCES

1. Seidman, E. B. Determination of sulfur oxides in stack gases. *Anal. Chem.* 30: 1680 (1958).